

Technology

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Determination of Formal Oxidation State of Co in MBE-Grown Co-doped TiO₂(001) Anatase Epitaxial Films by X-ray Absorption Spectroscopy

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INTRODUCTION

Diluted magnetic semiconductors (DMS) consist of nonmagnetic semiconducting materials doped with a few atomic percent of impurity magnetic cations. Magnetic coupling occurs by virtue of exchange interactions between the magnetic spins and free carriers in the semiconductor. The interaction can occur via *p-d* or *d-d* exchange, and can lead to antiferromagnetic or ferromagnetic coupling, depending on the concentration and the local structural environment of the magnetic impurity. DMS materials grown as thin epitaxial films can be used as spin injectors for semiconductor heterostructures, provided they are ferromagnetic.

Virtually all conventional DMS materials exhibit Curie temperatures of ~100K or less and must be *p*-type, which means that the exchange interaction leading to ferromagnetic behavior is hole mediated. Most of the effort expended to date on understanding the crystal growth and properties of thin-film DMS materials has focused on Mn-doped II-VI, III-V, and Group IV semiconductors.¹⁻⁴ Relatively little effort has gone into the investigation of “nontraditional” semiconductors, such as semiconducting oxides, to see if they are more robust magnetically. However, one such oxide - Co-doped TiO₂ anatase (Co_xTi_{1-x}O₂) - has recently been discovered to be the most magnetically robust DMS with regard to magnetic moment at saturation, coercivity, remanence, and Curie temperature.⁵ Indeed, it is one of the very few DMS materials demonstrated to exhibit ferromagnetic behavior above 300K. In addition, it has been shown that the material can be grown epitaxially by both pulsed laser deposition (PLD)⁶ and oxygen plasma assisted molecular beam epitaxy (OPA-MBE)⁵ on SrTiO₃(001) and LaAlO₃(001). However, the resulting magnetic properties differed considerably for the two growth methods, with significantly better properties exhibited by OPA-MBE grown material.

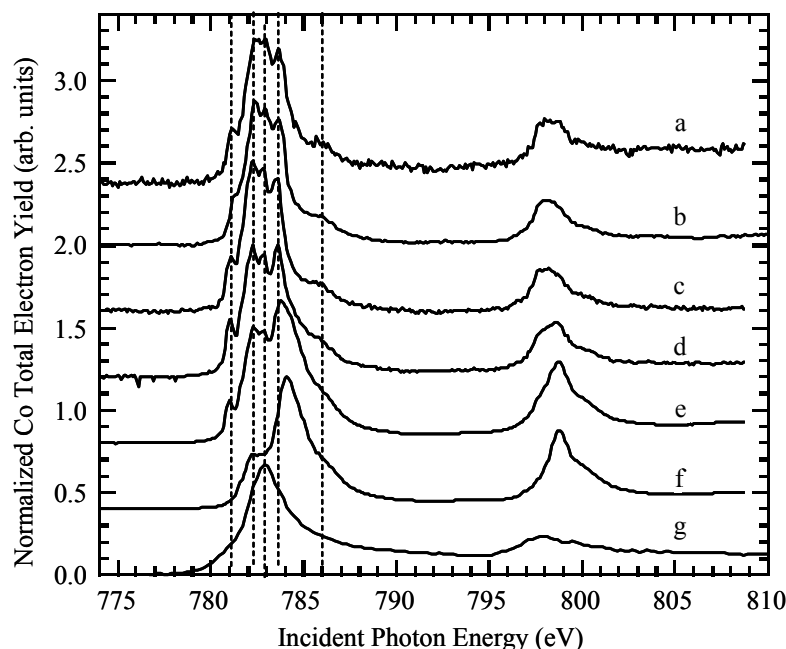
In order to understand the mechanism of magnetism in this fascinating material, it is essential to know the charge state of the magnetic cation (Co), and the doping type. We have utilized Co L-edge x-ray absorption spectroscopy (XAS) at beamline 9.3.2 to determine the Co charge state.

EXPERIMENT

Epitaxial Co_xTi_{1-x}O_{2-x} films of high structural quality were grown by OPA-MBE on LaAlO₃(001)⁷ using a system at PNNL described in detail elsewhere.⁸ The resulting samples were then transferred through air to beamline 9.3.2 and XAS measurements were made in total electron yield mode at the Co L-edge, Ti L-edge, and O K-edge. X-ray absorption near-edge spectra (XANES) were also recorded for several Co standards for comparison purposes. No surface cleaning was done, as the distribution of Co has been shown to be strongly modified by post-growth annealing at the temperatures required to rid the surface of carbon, or remove sputter damage.

RESULTS

We show in Fig. 1 Co L-edge XAS data for three films with different Co mole fractions (x) (Fig. 1a-c), and for standards containing Co in different oxidation states and local structural environments (Fig. 1d-g). The CoTiO_3 standard was a powder, CoO was a (001)-oriented bulk single crystal, $\gamma\text{-Co}_2\text{O}_3$ was a 100 nm thick (001)-oriented epitaxial film grown on $\text{MgO}(001)$ at PNNL, and the Co metal standard was a polycrystalline film evaporated *in situ* in the XAS chamber. Comparison of all film spectra with those for the standards reveals a good fit with both CoTiO_3 and CoO , which both contain Co^{+2} , but a very poor fit for both $\gamma\text{-Co}_2\text{O}_3$, which contains Co^{+3} , and for Co metal. The fit to CoTiO_3 is better than that to CoO . However, there is some similarity between the reference spectra for CoO and $\gamma\text{-Co}_2\text{O}_3$, particularly in the vicinity of the feature at 784 eV. This result indicates that there may be some Co^{+3} in the CoO single crystal. The very high degree of similarity between the spectra for the Co-doped anatase films and the CoTiO_3 standard establishes that Co in the former is in the +2 formal oxidation state. Interestingly, using the Co evaporation rate and oxygen plasma beam intensity we have used for the growth of $\text{Co}_x\text{Ti}_{1-x}\text{O}_{2-x}$ result in the epitaxial growth of metastable $\gamma\text{-Co}_2\text{O}_3$ on $\text{MgO}(001)$. Therefore, the anatase lattice stabilizes the formation of Co(II) , even though the conditions would result in Co(III) formation if pure Co oxide were allowed to grow under comparable



conditions.

Fig. 1 Co L-edge XAS for 20 nm thick films of epitaxial $\text{Co}_x\text{Ti}_{1-x}\text{O}_{2-x}$ on $\text{LaAlO}_3(001)$: (a) $x = 0.01$, (b) $x = 0.06$, (c) $x = 0.08$. Also shown are spectra for reference compounds containing Co in different formal oxidation states: (d) CoTiO_3 , (e) CoO , (f) $\gamma\text{-Co}_2\text{O}_3$, and (g) Co metal.

SIGNIFICANCE

Ion channeling measurements conducted at PNNL reveals that Co substitutes for Ti in the anatase lattice. Furthermore, Hall effect measurements carried out at PNNL show that these films are *n*-type semiconductors as grown, despite the fact that no intentional *n*-type doping was carried out. The origin of the *n*-type doping may have to do with the presence of H in the film,

which has been detected by ^{19}F nuclear reaction analysis at PNNL at a concentration that is of the same order of magnitude as that of the free carriers – 10^{19} to 10^{20} cm^{-3} . H may be the direct dopant, as occurs in $n\text{-ZnO}$.⁹ Alternatively, H_2 , which is present in the growth chamber at a very low partial pressure, may partially reduce lattice oxygen during growth to produce OH and a free donor electron according to the reaction $\text{O}^{2-}_{(\text{lattice})} + (1/2)\text{H}_2 \rightarrow \text{OH}^{-}_{(\text{lattice})} + \text{e}^{-}$. This phenomenon is currently under more detailed investigation.

It thus appears that Co-doped anatase TiO_2 is ferromagnetic by virtue of *electron* mediated exchange interaction between Co^{+2} cations that substitute for Ti^{+4} in the lattice. In order to maintain charge neutrality, each substitutional Co^{+2} must be accompanied by an O^{2-} vacancy. However, such vacancies are uncharged and therefore do not contribute any donor electrons. In fact, n -type semiconducting behavior and Co substitution are independent phenomena; some highly resistive films are nonmagnetic despite having several at. % Co. Indeed, the magnetization depends as much on the free carrier concentration as on the presence of substitutional Co, as expected for a DMS.

Significantly, virtually all other known DMS materials are ferromagnetic by virtue of *hole* mediated exchange interaction, which has been thought to be the stronger interaction.¹⁰ Therefore, Co-doped TiO_2 anatase is a highly unusual and potentially very important DMS in that it exhibits strong electron mediated exchange interaction at temperatures of at least 500K. No other known DMS exhibits these properties.

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Investigation of Surface and Bulk Half-metallic Character of Fe_3O_4 by Spin Resolved Photoemission

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The existence of a new class of magnetic materials displaying metallic character for one electron spin population and insulating character for the other was first postulated by DeGroot *et al* [1] in 1983 based on theoretical band structure calculations of the ferromagnetic Heusler alloy NiMnSb. Since then such half metallic materials, which by definition possess 100% electron polarization at the Fermi energy have attracted considerable theoretical, experimental, and technological interest as potential pure spin sources for use in spintronic devices [2], data storage applications, and magnetic sensors. In addition to Heusler alloys half metallic character has also been predicted to occur in a wide range of manganites [3], metallic oxides [4], and CMR systems [5]. However, such predictions have proven to be extremely difficult to confirm experimentally [6]. A major factor in this failure has proven to be significant experimental challenges in obtaining a clean stoichiometric surface with a magnetization that is truly representative of the bulk material and thus suitable for further study by magneto-optical or spectroscopic techniques.

In recent experiments at the ALS we have used spin resolved photoemission to study the role that surface reconstruction plays in the observed polarization of the half metallic candidate material magnetite, Fe_3O_4 . Magnetite has a structure that is relatively simple in comparison to most other candidate half metals and it can be grown epitaxially using conventional deposition techniques [7], making it one of the strongest candidates for spintronic applications. However previous spin resolved measurements have shown that the polarization at the Fermi edge is only ~40% [8] rather than the anticipated 100%.

By conducting spin resolved depth profile measurements and comparing the results to theoretical band structure calculations we have demonstrated that Fe_3O_4 exhibits a semiconducting non-magnetic surface re-construction which significantly reduces the observed polarization but that, in contrast, the underlying bulk material is in fact very strongly polarized. Indeed, once the effects of this surface reconstruction are taken into account by theoretical models of the polarization an excellent match is obtained between the experimental spin resolved spectra and simulated spectra generated from theoretical spin polarized band structure calculations [9] (fig. 1). Hence our results strongly support the notion that Fe_3O_4 is indeed a half-metallic material suitable for use in a new generation of spintronic devices.

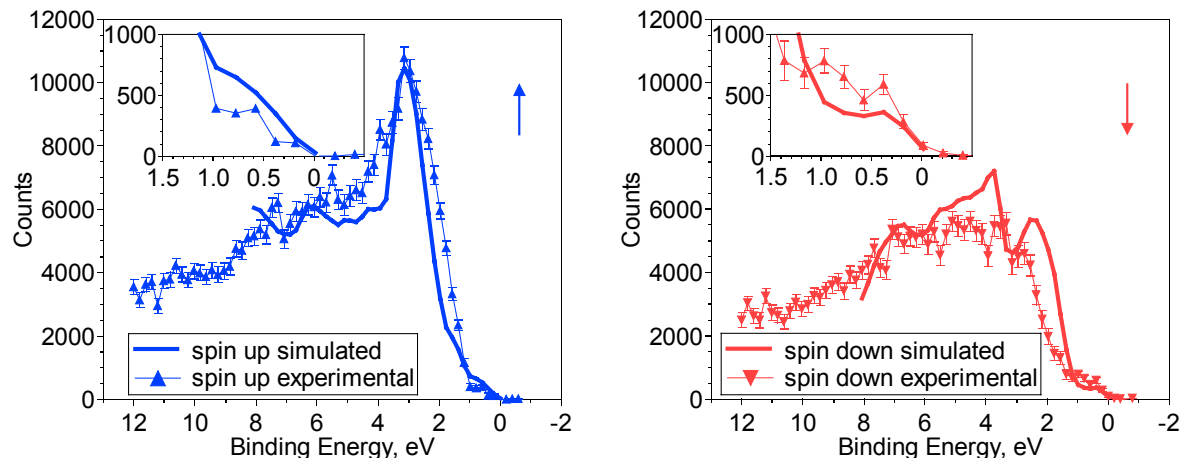


Figure 1

Comparison of experimental spin resolved Fe_3O_4 valence bands with equivalent simulated spectra derived from theoretical calculations that have been corrected to account for the presences of a nonmagnetic surface reconstruction

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Magnetic Circular Dichroism in the X-ray Absorption Spectra of the CMR Compound, $\text{Yb}_{14}\text{MnSb}_{11}$

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This work is part of ongoing investigations into the magnetic and electronic properties of the rare-earth transition metal Zintl phases $\text{A}_{14}\text{MnPn}_{11}$ ($\text{A} = \text{Eu}, \text{Yb}$; $\text{Pn} = \text{Sb}, \text{Bi}$) at the Advanced Light Source. We have recently obtained exciting new results from X-ray magnetic circular dichroism (XMCD) investigations of the $\text{Yb}_{14}\text{MnSb}_{11}$ system. Specifically, we have used XMCD as an element specific probe into the nature of the magnetic moment in this system with the intention of exploring the proposed half-metallic nature of this compound and its related substitutional analogues. Our XMCD measurements indicate that $\text{Yb}_{14}\text{MnSb}_{11}$ is a half-metallic ferromagnet, and we have submitted our results for publication to Physical Review Letters.

The term half-metallic ferromagnet arises from theoretical predictions made by R.A. de Groot et al based on band structure calculations of the ferromagnetic Heusler alloy NiMnSb .¹ These calculations proposed a new phase of matter that displays separate electronic properties for majority-spin and minority-spin electrons. Specifically, one electron spin population is metallic and the other is insulating. Such a material, (possessing 100% spin polarization of the conduction electron) would hold significant technological potential as a single-spin electron source for spintronic devices, data storage applications, and high efficiency magnetic sensors.²

The materials we are studying are new compounds that belong to a class of materials called transition-metal Zintl phases. These compounds are isostructural to $\text{Ca}_{14}\text{AlSb}_{11}$ and crystallize in the tetragonal space group $I4_1/a$ ($Z = 8$). The $\text{Yb}_{14}\text{MnSb}_{11}$, $\text{Yb}_{14}\text{MnBi}_{11}$ and $\text{Eu}_{14}\text{MnSb}_{11}$ analogues are each reported to order ferromagnetically at 56 K, 58 K and 28 K, and 92 K, respectively.³⁻⁶ $\text{Eu}_{14}\text{MnBi}_{11}$ is an antiferromagnet with a Néel transition at $T_N = 32$ K.⁶ Each of these materials exhibits a large resistance drop associated with their unique magnetic ordering temperature. This behavior is attributed to colossal magnetoresistance effects, and could help support the proposal made by Pickett and Singh of a correlation between half-metallicity and colossal magnetoresistance.⁷ These systems are ideal for investigations into the links between magneto-resistance, magnetic moment and half-metallic behavior.

The ability to perform X-ray magnetic circular dichroism experiments on the EPU has allowed us to probe the dichroic characteristics of Mn and Sb in the $\text{Yb}_{14}\text{MnSb}_{11}$

system during experiments recently performed on beamline 4.0 of the ALS. Figure 1 shows the results from XMCD experiments on the Mn L_{23} , Sb M_{45} , and Yb N_{45} edges of $\text{Yb}_{14}\text{MnSb}_{11}$. A dramatic dichroism effect is shown in the Mn L_{23} region which is confined to one sub-component of the Mn edge and closely matches theoretical models for Mn^{2+} , d^5 dichroism (Figure 1d). The difference in intensity upon change of helicity is greater than 30%, and is strong evidence of a significant moment being present on the Mn. In contrast, no dichroism was observed in the Yb edges, but a small antialigned moment is present in the Sb M_{45} edges as shown on the left side of Figure 1. This result is surprising because initial models predicted that dichroism would be restricted to the Mn L_{23} region (with no dichroism in the Sb M_{45} region) and that it would be Mn^{3+} , d^4 like in character. However, an ongoing collaboration with theoretical groups in the physics departments of the University of California, Davis and the University of Illinois, Urbana to model the Ca and Ba analogues of this structure type has now produced calculated results consistent with our experimental observations of how the Sb behaves in this system. They argue that the Mn should be in a $2+$, d^5 configuration, and the Sb_4 cage surrounding the Mn should have a hole antialigned to the Mn moment giving a total moment of $\sim 4 \mu_B/\text{formula unit}$. Our experimental results are consistent with these new theoretical results, and in addition, these comparisons of data with theoretical calculations and SQUID magnetometry measurements confirm that $\text{Yb}_{14}\text{MnSb}_{11}$ is indeed a half-metallic ferromagnet.⁸⁻¹⁰

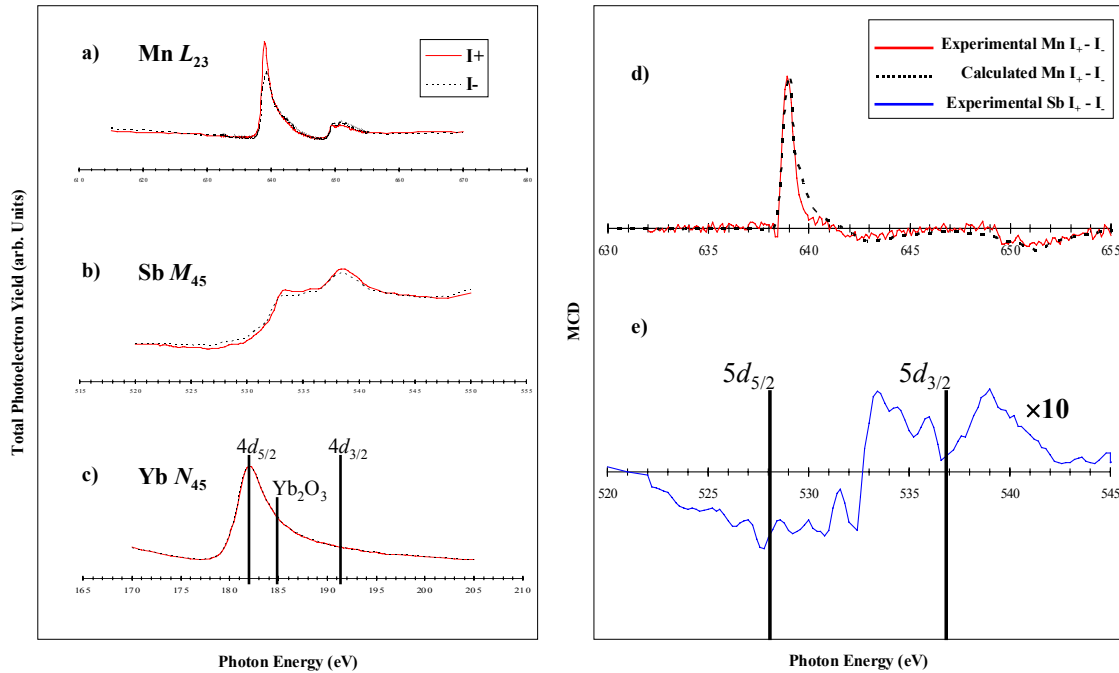


Fig. 1. The raw absorption spectra at plus and minus light polarization for a) Mn L_{23} , b) Sb M_{45} , and c) Yb N_{45} are shown on the left. The XMCD spectra for d) the experimental Mn L_{23} denoted by a solid red line and the calculated Mn^{2+} , d^5 L_{23} denoted by a dashed black line, and e) the experimental Sb M_{45} denoted by a solid blue line.¹⁰

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Photoemission Electron Microscopy and X-Ray Magnetic Circular Dichroism of $\text{Fe}_x\text{Ni}_{(1-x)}$ Thin Films on Cu(111)

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INTRODUCTION

Our research focuses on controlling the structure, composition and the resultant magnetic properties of metal alloy thin film growth at the atomic level. Better understanding and control of surface/interface magnetism is relevant to the application of the giant magneto-resistive effect to read heads for magnetic recording. We have studied $\text{Fe}_x\text{Ni}_{(1-x)}$ alloy thin films for their technological relevance to the above mentioned technology. The dependence of the magnetism on the stoichiometry x is one of the questions of interest. In addressing this problem, the structure of the thin film must be also considered. In terms of crystal structure, a well known “Invar effect” exists in bulk FeNi alloy because of structural incompatibilities of the two elements. Pure Fe is stable in bcc phase whereas pure Ni has fcc structure. A bulk alloy containing more than 65% Fe transforms to bcc by a Martensitic transformation, and the magnetization falls to zero. In thin film alloys, the problem may become more complex because of the effect of substrate structure and interface properties. On the other hand, how this structural change affects the magnetic order in the film is not well known. A simultaneous study of film structure, magnetic structure and magnetism is needed to better understand the system.

Several studies on $\text{Fe}_x\text{Ni}_{(1-x)}$ alloy thin films have been reported^{1,2,3,4}. Information on the growth, structure, and magnetic moments as a function of thickness and concentration has been obtained using various techniques such as low energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED), photoelectron diffraction, surface magneto optical Kerr effect (SMOKE), X-ray magnetic linear dichroism (XMLD), Mossbauer spectroscopy, and superconducting quantum interference device (SQUID) magnetometry. We have used the photoemission electron microscope (PEEM2) at the Advanced Light Source (beamline 7.3.1.1) to study this film system. PEEM has the unique capability of imaging the film’s magnetic structure with high spatial resolution and elemental specificity. Simultaneously, quantitative magnetic information can be obtained using magnetic circular dichroism in X-ray absorption spectroscopy. At two different thicknesses, we have made sixteen samples and studied the dependence of magnetic structure on varying Fe concentration and substrate quality ($x = 0, 0.28, 0.55, 0.6, 0.66, 0.74, 1.0$ at $10\text{\AA} \approx 5\text{ML}$, $x = 0.9, 0.25, 0.33, 0.42, 0.5, 0.55, 1.0$ at $20\text{\AA} \approx 10\text{ML}$). We have observed clear ferromagnetic domain structures of the film on a Cu(111) surface for $x \leq 0.60$ at room temperature.

RESULTS

Samples with high Fe content ($x=0.66, 0.74$ at 5ML) have been observed to be non-magnetic at room temperature. All other alloy samples ($x \leq 0.6$, 5ML and 10ML) showed clear ferromagnetic contrast. This trend of reduction in Curie temperature at higher Fe concentration is also observed by spin resolved photoemission spectroscopy measurements carried out at the Advanced Light Source (beamline 7.0.1.2). A pure Ni film at 5ML thickness was non-magnetic at room temperature. According to a SMOKE measurement, 5ML is approximately the thickness where the Curie temperature becomes less than room temperature for Ni/Cu(111)⁵.

Fig. 1 shows typical ferromagnetic images with a $12\mu\text{m}$ field of view for a 5ML thick $\text{Fe}_{0.6}\text{Ni}_{0.4}$ film on Cu(111). Each image is obtained by dividing an image acquired at the L3 Fe (or Ni) edge by one acquired at the L2 Fe (or Ni) edge. The images show alignment of the magnetic domains for

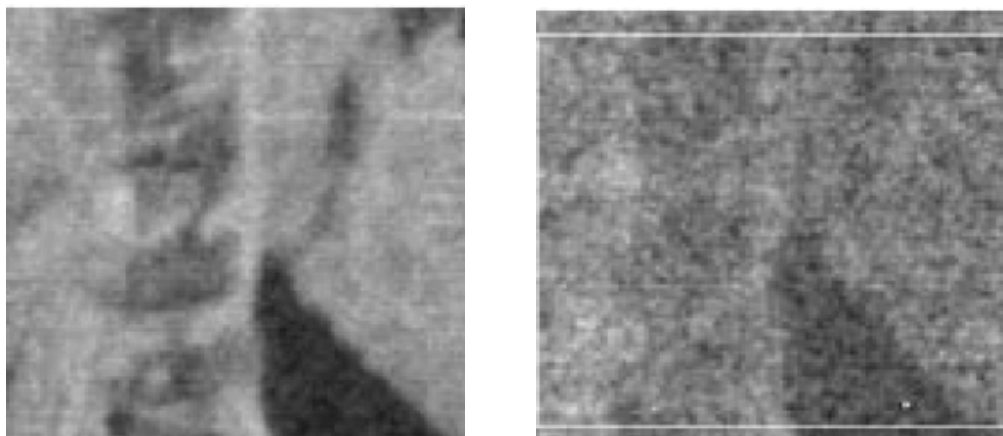


Fig. 1. XMCD ferromagnetic images with a $12\mu\text{m}$ field of view for a 5ML thick $\text{Fe}_{0.6}\text{Ni}_{0.4}/\text{Cu}(111)$. Left: Fe XMCD contrast, Right: Ni XMCD contrast.

Fe and Ni, suggesting that Fe and Ni form a good alloy on this surface. By comparing the images shown in Fig. 2 and Fig. 3, we find a clear dependence of the domain structures on film thickness and substrate quality. Fig. 2 shows magnetic contrast images of 5ML alloy films on a mechanically polished substrate. On these samples, observed magnetic structures appear to correlate to surface topographic features. No regular appearance of domain structure was seen. Comparison of the image at the pre-absorption edge, which shows only topographic contrast, with the magnetic contrast image clearly shows the correlation between surface structural features and the formation of magnetic domains. An experiment showed that magnetic contrast observed at room temperature disappears gradually upon heating. Contrast is recovered again as the sample temperature is lowered below the Curie temperature. This also confirms the relation between domain structure and surface geometric structures. These observations are consistent for each 5ML sample analyzed. In contrast, for 10ML films on an electropolished substrate as shown in Fig. 3, pinning due to surface defects is observed less frequently. Magnetic structures and textures appear to be more uniform and the sizes of the structures were smaller and on the order of $1\text{-}3\mu\text{m}$. At the alloy composition of $x=0.44$, regular, periodic appearance of larger domain structures ($5\text{-}10\mu\text{m}$ width and $70\mu\text{m}$ length), defined by 180° domain walls, are observed, as shown in Fig. 4. By observing the two images shown in Fig. 4, we conclude that alloy film at this composition and thickness show in-plane magnetization.

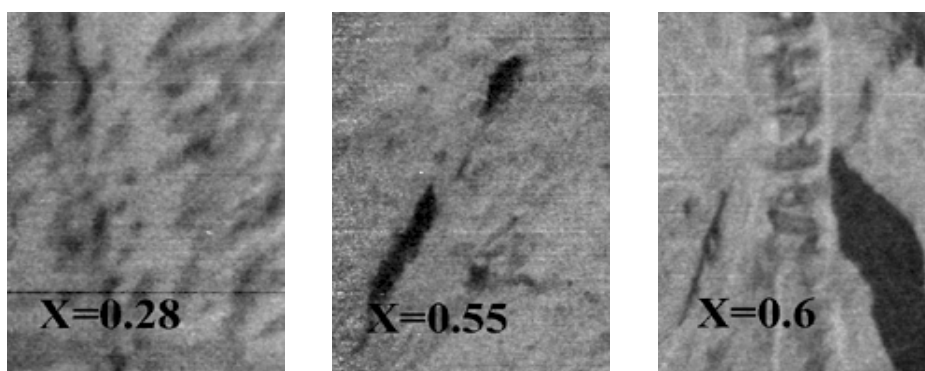


Fig. 2. XMCD ferromagnetic images with $H22\mu\text{m} \times V30\mu\text{m}$ field of view for 5ML films with varying Fe composition x .

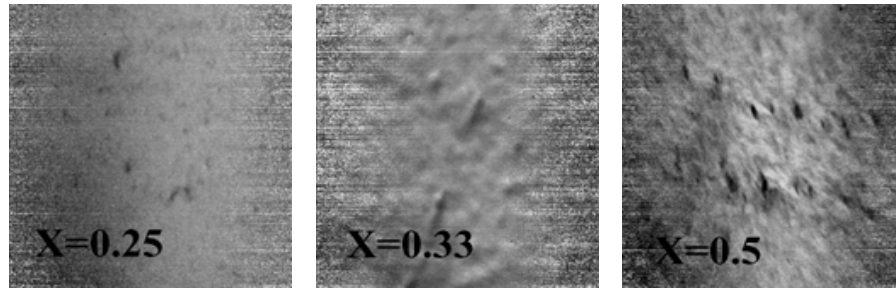


Fig. 3. XMCD ferromagnetic images with $65\mu\text{m} \times 65\mu\text{m}$ field of view for 10ML films with varying Fe composition x .

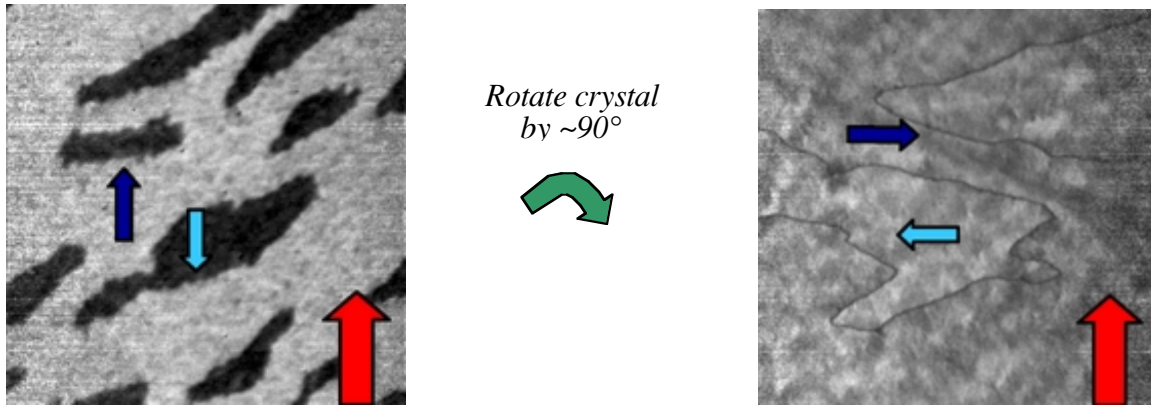


Fig. 4. XMCD ferromagnetic images with Right: $45\mu\text{m} \times 45\mu\text{m}$ and Left: $45\mu\text{m} \times 45\mu\text{m}$ field of view for 10ML thick $\text{Fe}_{0.56}\text{Ni}_{0.44}/\text{Cu}(111)$. Smaller arrows indicate the magnetization direction and larger arrows show the direction of the incident photon momentum.

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Recent achievements with magnetic soft X-ray microscopy at XM-1

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INTRODUCTION

Studies of magnetic domain structures in systems of low dimensionality are a major issue both from a fundamental physics point of view and in a technologically relevant context. The systems of interest are thin single or stacked multicomponent multilayered magnetic films and are often laterally patterned micro- and nanostructures. Though a large number of imaging techniques is established the outstanding challenge they have to meet, is a layer-resolved (e.g. via chemical sensitivity) spatio-temporal recording of the switching behavior of the magnetic domain structure as this determines largely the technological functionality. Supported by intensive micromagnetic simulations a comprehensive fundamental understanding and a subsequent potential design of the magnetic domain structures is essential.

X-ray magnetic circular dichroism (X-MCD) yields at element-specific spin-orbit coupled (e.g. $L_{3,2}$ and $M_{5,4}$ absorption edges large values up to 50%. In combination with soft X-ray transmission microscopy this serves as huge magnetic contrast mechanism to image magnetic domain structures at a resolution down to 25nm provided by Fresnel zone plate optics (magnetic soft X-ray transmission microscopy (M-TXM)) [1,2]. A description of the technique is found elsewhere [3]. Here we report the recent achievements by selected examples taken at the XM-1 beamline at the ALS/Berkeley CA.

RESULTS

In Fig. 1 the domain pattern of an amorphous 59nm thin $Gd_{25}Fe_{75}$ film with a pronounced perpendicular anisotropy is shown. The images have been taken at the Fe L_3 (a) and the Gd M_5 (b) edge thus probing the local magnetization of Fe and Gd, resp., in an element-specific manner. Though at these two edges the spin-orbit coupling is both parallel the observed reversal of magnetic contrast reflects the antiparallel 3d-4f coupling and proofs the magnetic character of the structures.

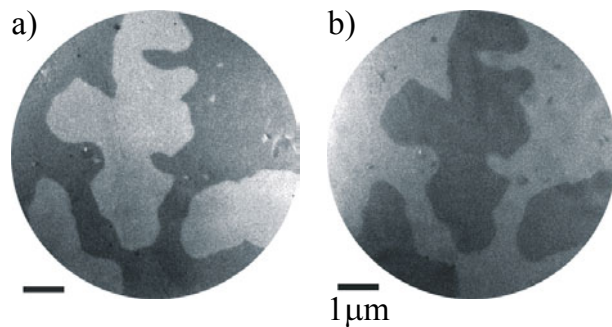


Figure 1 Domain structure of a $Gd_{25}Fe_{75}$ film taken at the Fe L_3 (a) and the Gd M_5 (b) edge.

The magnetization switching can be addressed by recording the domains within complete hysteresis loops. In Fig. 2 a (0.4nmFe/0.4nmGd)x75 multilayered system with lithographically

written line elements with a width of 300nm emerging from a continuous film were studied at saturation (a) and at an applied magnetic field perpendicular to the films surface of 4kOe (b). The maze pattern observed in the continuous film starts penetrating from the left side of the image into the GdFe line structures as a straight line domain. A corresponding white line domains emerges from the right. If the sense of rotation from up to down does not fit for both domains, the melting of these two domains is blocked until at a higher magnetic field finally they are forced to form one single line. As can be seen in the third line from the bottom this is not always the case.

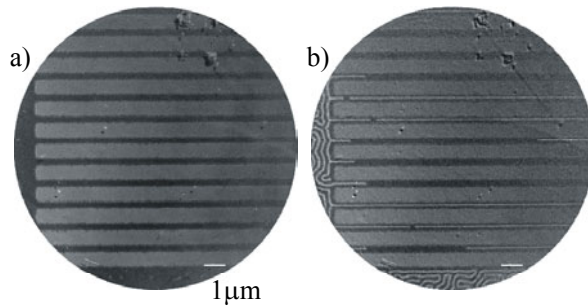


Figure 2 Domain structure in a lithographically edged line pattern (width 300nm) of a multilayered 75x(0.4nm Fe/ 0.4nm Gd) system. a) saturated state, b) domain structure at 0.4kOe.

As the dichroic contrast is given by the projection of the magnetization onto the photon propagation direction both in-plane and out-of-plane systems can be imaged. Amorphous Terfenol-D ($\text{Fe}_{66.5}\text{Tb}_{9.5}\text{Dy}_{24.0}/2\text{at}\%\text{Zr}$) layers exhibit an anisotropy perpendicular to the film plane as they are far from thermodynamically equilibrium.

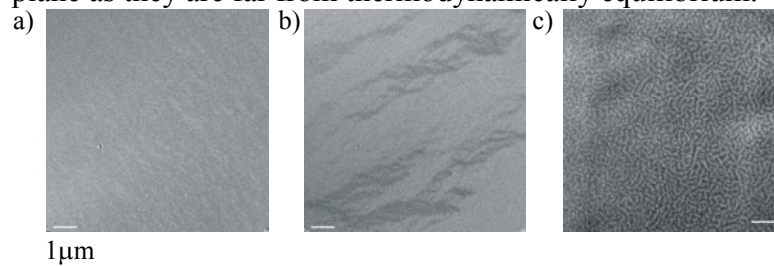


Figure 3 Magnetic domains in Terfenol-D recorded at the Fe L_3 edge in-plane (a,b) and out-of-plane (c).

However, thermal treatment at elevated temperatures (about 500-600K) forces the anisotropy into the film plane. In Fig. 3a) and b) the results obtained with a 70nm thin sample thermally treated at 500K are shown. A typical in-plane domain pattern can be observed if the magnetic field applied along the sample surface and horizontal in the paper plane is increased from 0 Oe (a) to 200 Oe (b). The corresponding domains for the non-tempered (out-of-plane) system are shown in (c).

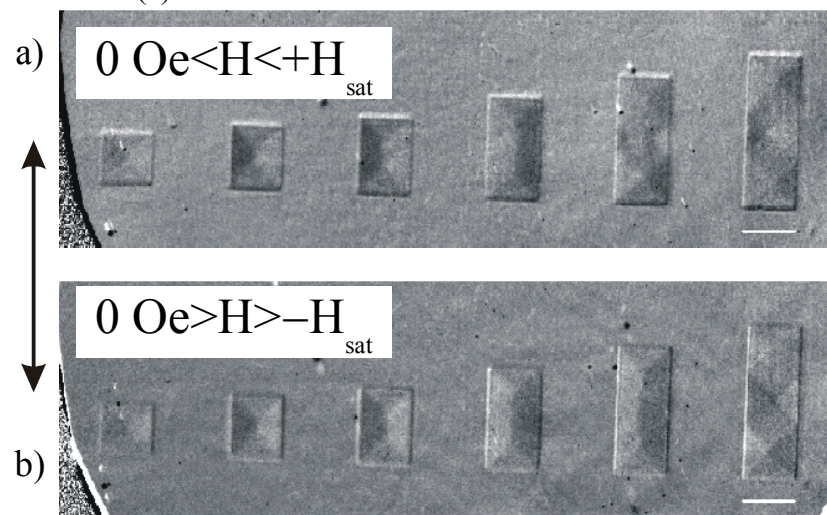


Figure 4 Variation of the domain patterns with size in 50nm thick Permalloy ($\text{Fe}_{20}\text{Ni}_{80}$) nanostructures. Field direction along the vertical direction (see arrow). The bar is 1μm. The bar is 1μm.

Results of the magnetic domain structure recorded at the Ni L₃ edge within varying external magnetic fields in 50nm thin PY (Permalloy Fe₂₀Ni₈₀) patterned elements are shown in Fig. 4. The variation of the domain pattern with varying aspect ratio (width to height) between 1 and 3 is clearly visible. In Fig. 1a) and b) the field direction was along the fixed width of 1µm. Up to an aspect ratio of 1.5 a single closure domain pattern appears, while a more complex configuration (cross tie wall) emerges for larger aspect ratios.

OUTLOOK

An outlook to the potentials of M-TXM is time dependent imaging where the inherent pulsed time structure of the synchrotron light in the sub-nanosecond regime will be used to study spin dynamics.

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Spin-resolved electronic structure studies of ultrathin films of Fe on singular and vicinal GaAs

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Recently, there has been considerable interest in the study of spin injection at ferromagnetic semiconductor heterojunctions and ferromagnetic metal – semiconductor contacts^{1,2,3,4}. Studies of n-type semiconductors have demonstrated spin-coherent transport over large distances⁵ and the persistence of spin coherence over a sizeable time scale⁶. Clearly such investigations have been stimulated by the potential of the development of ‘spintronics’, electronic devices utilising the information of the electron spin states. To understand and improve the magnetic properties of ultrathin Fe films on GaAs has been the aim of many research groups over recent years. The interest in this system has both technological and fundamental scientific motivations. Technologically, Fe on GaAs may serve to realize spin electronic devices. From a fundamental science point of view, Fe on GaAs serves as a prototype for studies of the interplay between the crystalline structure and morphology of an ultrathin film, its electronic structure and the long range magnetic order it exhibits.

In contrast to the attention given to Fe on variously prepared GaAs substrates, the magnetism of Fe on vicinal GaAs substrates has received scant attention. This in spite of the fact that films grown on vicinal substrates present a number of advantages and opportunities. For example, they are known to exhibit enhanced structural homogeneity, surface diffusion tends to follow well mapped patterns (the quasi-periodicity has been exploited to produce quantum wires) and there is an additional degree of control of the film growth beyond those associated with temperature and substrate surface composition⁷.

In a preliminary combined spin-polarized secondary electron spectroscopy, photoelectron spectroscopy and LEED study (carried out on the SRS, Daresbury Laboratory) of the remanent magnetic properties of Fe on singular and vicinal (3° offset) GaAs we have shown both that the various magnetic phases formed are dependant upon the Ga to As surface composition of the substrate and that they evolve in characteristic (but not well understood) ways with Fe overlayer thickness⁸. A remarkable feature in this system, which illustrates the importance of the Fe overlayer/substrate interaction, is the magnetic anisotropy; the easy axis of the Fe films on Ga-terminated substrates is perpendicular to that for As-terminated substrates^{9,10}.

These measurements were followed up with combined spin-resolved photoemission and magnetic linear dichroism experiments on Fe deposited on vicinal (offset by 3° and 6°) or singular GaAs substrates on Beamline 7 at the ALS in collaboration with Elaine Seddon of CCLRC Daresbury Laboratory, Dan Waddill of The University of Missouri-Rolla and James Tobin Of Lawrence Livermore National Laboratory. The GaAs(100) substrates were available for film deposition at room temperature after substrate decapping *in-situ* (by thermal annealing),

at the ALS. By mounting both singular and vicinal GaAs substrates on the same sample tile the same growth conditions applied for both films facilitating direct comparison. The surface quality was monitored using LEED. The following data were obtained, high resolution spin-integrated valence bands, the spin-resolved valence bands and their energy dispersion, the film thickness dependence of the spin-resolved valence bands, magnetic linear dichroism data on the Fe3p and Fe2p core levels at a variety of photon energies.

The experiments, which were performed with Dr. Simon Morton and Dr. Jim Tobin in November of 2000 have produced considerable amount of interesting results. The significant differences in the spin-resolved valence bands between *ca.*20 Å thick Fe films on singular and vicinal (3°) GaAs are illustrated in Fig.1. As the terrace width is *ca.*55 Å the spectral differences are not due to step-localized features.

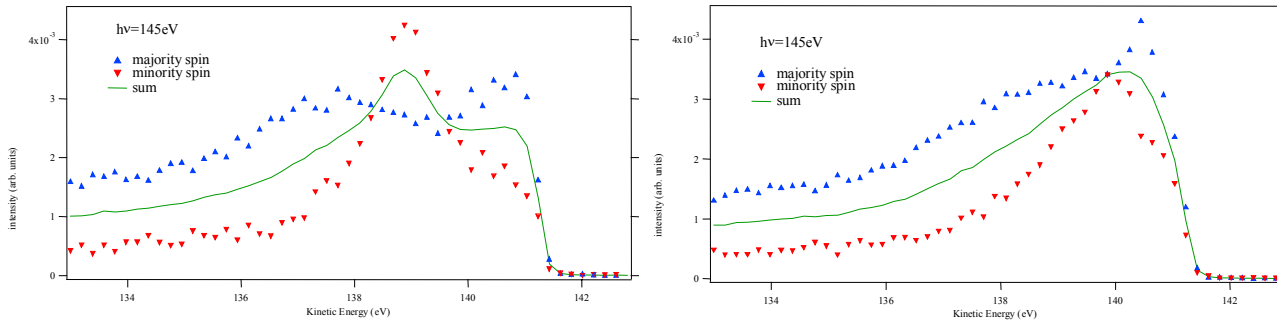


Figure 1
Spin-resolved valence band photoemission results for Fe on singular GaAs (left) and Fe on vicinal (3°) GaAs (right).

Other interesting results include the following. At low film thicknesses, Fe deposited on singular substrates was found to have a lower Curie temperature than Fe on vicinal substrates. Fe deposited on singular substrates reveals a larger energy dispersion of the spin-resolved valence bands than Fe on vicinal substrates. Only marginal differences can be seen between the spin-resolved valence bands of Fe deposited on 3° stepped GaAs substrates and Fe deposited on 6° stepped GaAs substrates. Also, in contrast to the valence band studies, the linear magnetic dichroism results obtained for these samples are very similar.

Further experiments at ALS during oct 2001 enabled us to obtain considerably more interesting results. Whilst the detailed analysis of the results is still underway, Fig.2 shows a large contrast of the valence band spectra of Fe versus incident photon energy between that on a singular and a vicinal substrate. The strong feature on the left in Fig.2 was found to be sensitive to the thickness of the Fe layer and the origin of which is still not yet clear at the present stage.

In summary, the experiments at the ALS have been extremely rewarding. They have answered some questions, clarified our thinking on others and raised yet other questions for which we have no answers at the moment. The run has, however, shown that further access to the ALS is needed to fully understand this fundamental and technologically important system.

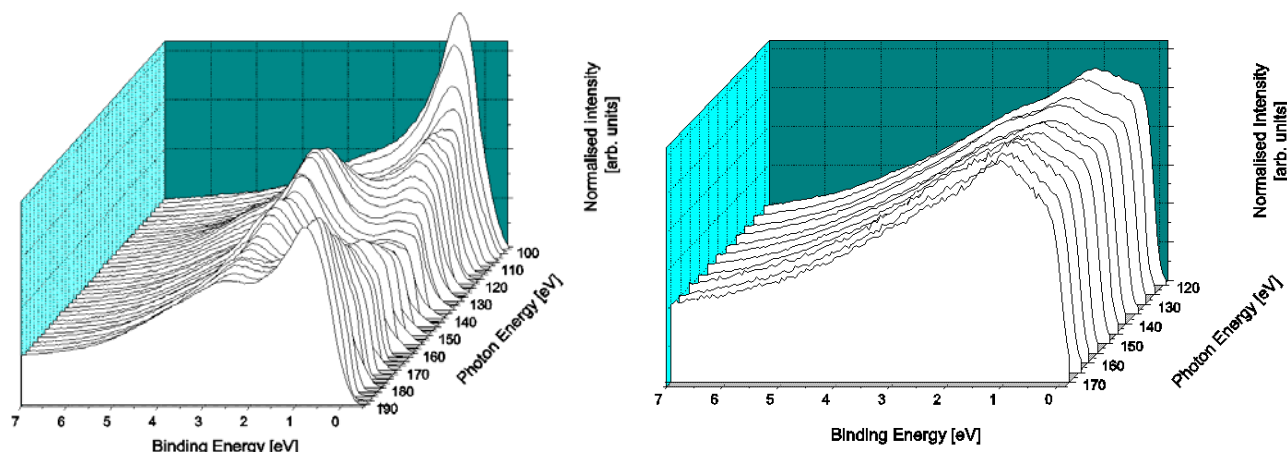


Figure 2.

Valence band spectra of Fe, normalised to the secondary electron tails, versus photon energy for films on singular substrate (left) and on 6 degree vicinal substrate (right).

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